(12) **UK Patent Application** (19) **GB** (11) **2 237 291** (13) **A**

(43) Date of A publication 01.05.1991

(21) Application No 8921459.7

(22) Date of filing 22.09.1989

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(51) INT CL[5]
C25D 1/00, G01N 27/12

(52) UK CL (Edition K)
C7B BDEE B113 B128 B283 B506 B518 B797
G1N NCGF N19B2Q N19F7B
U1S S1496 S1497 S1502 S1510 S2176 S2192

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(58) Field of search
UK CL (Edition J) C7B BBRA BBRB BBU BDEE BDFA BDFD BDFE BDFK BDHR BDJA BDKA BDKD BDKE BDNA BGAX, G1N
INT CL[4] C25D, G01N
Online databases: WPI, CLAIMS

(54) **Method of bridging gaps in a substrate by electrodeposited film, for use in gas sensor manufacture**

(57) A film of material is formed on a substrate 1 having an aperture 2 by electrochemically depositing from an electrolyte a film 12 of material onto an electrode 3a, 3b on the substrate and onto an adjoining electrode which extends over the aperture on one side of the substrate such that the film adheres to, and bridges the aperture in, the substrate. The deposited film is then separated from the adjoining electrode in the region of the aperture to leave the film substantially intact, adhering to the substrate and bridging the aperture. The method of film formation may be employed to deposit polymeric gas sensing films on substrates for use in gas sensors by floating the substrate on a mercury anode 6 on which floats electrolyte 7 comprising potassium chloride and pyrrole monomer and passing current between the mercury anode and cathode 7. The resulting sensor has a larger area film and is more sensitive than conventional sensors.

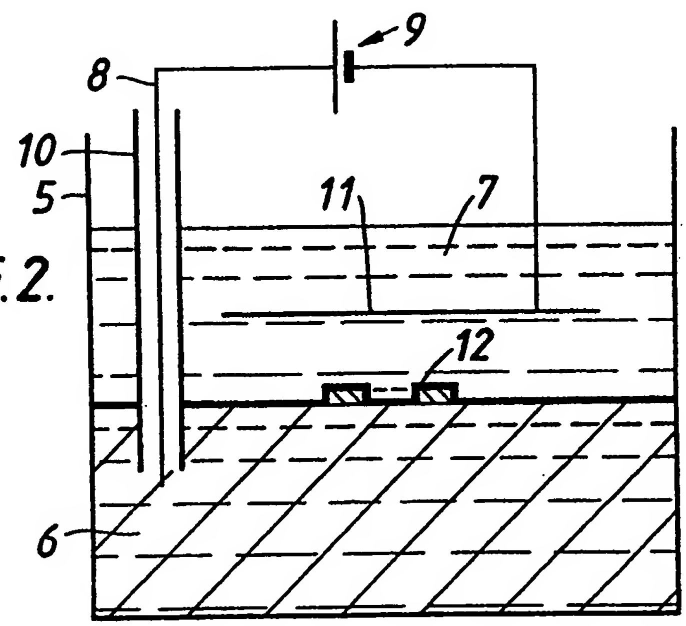

FIG. 2.

At least one drawing originally filed was informal and the print reproduced here is taken from a later filed formal copy.

This print takes account of replacement documents submitted after the date of filing to enable the application to comply with the formal requirements of the Patents Rules 1990.

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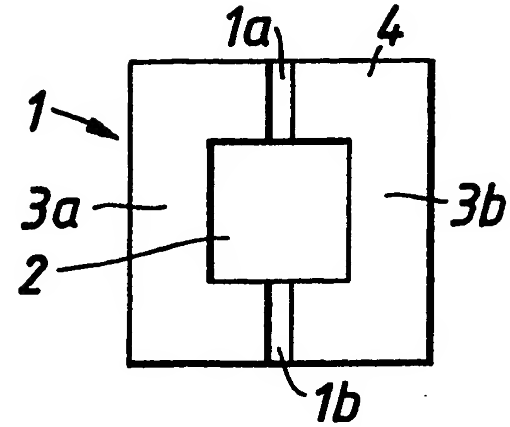

FIG.1.

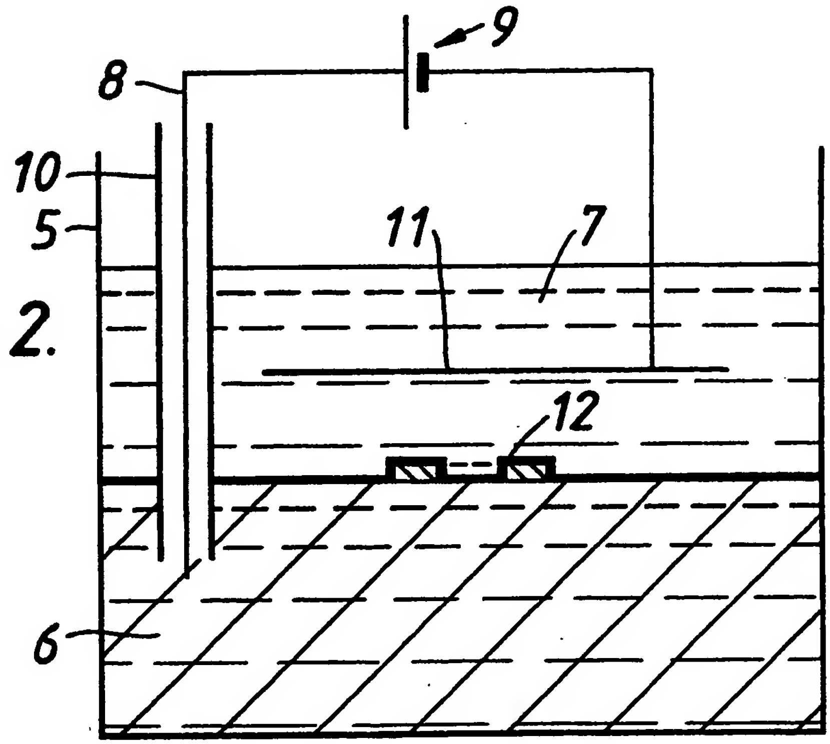

FIG.2.

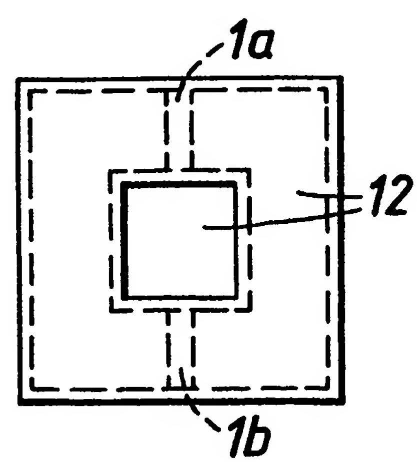

FIG.3.

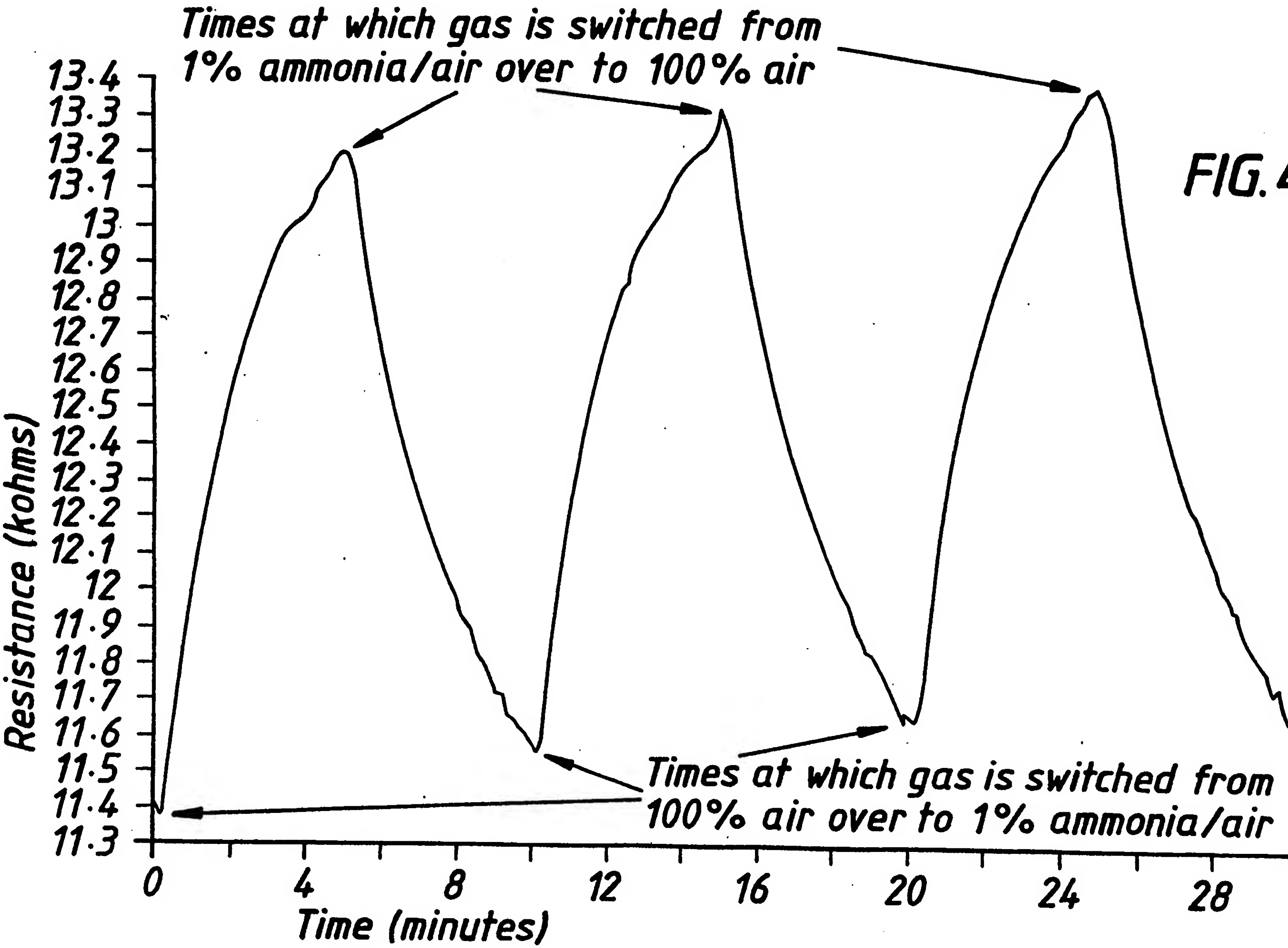
Times at which gas is switched from
1% ammonia/air over to 100% air
Times at which gas is switched from
100% air over to 1% ammonia/air
Resistance (kohms)
13.4
13.3
13.2
13.1
13
12.9
12.8
12.7
12.6
12.5
12.4
12.3
12.2
12.1
12
11.9
11.8
11.7
11.6
11.5
11.4
11.3
0
4
8
12
16
20
24
28
Time (minutes)

FIG. 4.

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FORMING A FILM OF MATERIAL ON A SUBSTRATE

The invention relates to the formation of films on substrates and, more particularly, to a method of forming a film of material on a substrate having an aperture or gap therein.

One subject matter field to which the invention is especially applicable is that of gas sensors. It has previously been proposed that gas sensing components may ultilise organic polymers which are long unsaturated systems and have an electrical conductivity of the order of that found in semiconductors such as silicon or germanium. Such polymers may have either an excess or deficiency of electrons to provide negative or positive charge carriers which confer n- or p- type semiconducting characteristics.

In order to make such polymers more specific or sensitive to a particular gas inorganic or organic "counter ions" have been incorporated into the polymer structure. These polymers can interact with gases, particularly oxidising or reducing gases. Such interaction alters the density of charge carriers and thus the electrical conductivity of the polymer. This effect can be used as a basis of a method of detecting gases since by altering the 'counter ion' in the polymer the sensitivity may be tuned to a particular gas such as methane, carbon monoxide or

nitrogen oxides.

One prior known method of producing a gas sensor component utilizing a film or layer of organic polymer, such as poly-pyrrole comprises immersing an electrically insulating substrate, eg. in the form of a solid tile, into an electrolyte solution containing the monomer of the polymer, such as pyrrole, and potassium chloride. The tile has on its surface a pair of electrodes defining a narrow gap therebetween. An electric current is then passed between another electrode immersed in the electrolyte and the substrate electrodes which together form the anode. This leads to oxidation and polymerisation of the monomer and to electrochemical deposition of the polymer on the substrate to form the film. Initially the polymer film forms on the substrate electrode surfaces (ie. the anode surfaces) only but subsequently builds up sufficiently to bridge the gap and provide a small strip of polymer between the electrodes which forms the active part of the gas sensor component.

One disadvantage of the above described method of forming a film on a substrate is that only one side of the resulting film is accessible and this may limit its sensitivity to a gas to be detected when used in a gas sensor.

An object of the present invention is to provide a method of making a substrate having a film which is accessible from both sides.

To this end, according to the invention a method of forming a film of material on a substrate having an aperture or gap therein, comprises electrochemically depositing from an electrolyte a film of material onto an electrode on the substrate and onto an adjoining electrode which extends across the aperture or gap in the substrate such that the film adheres to, and bridges the aperture or gap in, the substrate, and then separating the deposited film and electrode in the region of the aperture or gap in which the film has deposited from each other to leave the film substantially intact, adhering to the substrate and bridging the aperture or gap in the substrate.

The electrode in the region of the aperture or gap, or a support therefor, may be co-extensive with the substrate and such electrode may contact one side of the substrate.

Preferably, the electrode in the region of the aperture or gap is formed by a surface region of a pool of mercury on which the substrate is supported and the electrolyte floats. The substrate may be supported by the mercury itself, that is the substrate may float on the mercury.

Conveniently, the electrode on the substrate may comprise spaced electrical conductors over which the film forms. For example, the spaced electrical conductors may comprise electrically conducting material which has been deposited on areas of the substrate, such as by sputtering, screen printing or electron etching, prior to the electrochemical deposition of the polymer. The presence of the spaced conductors facilitate incorporation of the resulting substrate supported film into an electrical arrangement if required. For example, electrically conducting means, e.g. wires, may be connected subsequently to the electrical conductors to connect the substrate/film composite into an electrical arrangement.

Preferably, the electrolyte contains the monomer of an organic based unsaturated polymer and the unsaturated organic based polymer is the material which is electrochemically deposited to form the film. The electrolyte may contain electrically charged species which are incorporated in the electrochemically deposited film and are electrically balanced in the film by the presence of oppositely charged polymer components. For example, the monomer may be pyrrole and the organic based unsaturated polymer is polypyrrole, whilst the electrically charged species in the electrolyte and the formed film may be anions such as, chloride anions. The

balancing positive charges in the polymer film can be considered to provide mobile 'holes' which impart p-type semiconductivity to the film.

Subsequent to separating the polymer film from the electrode into the region of the aperture or gap, the film may be electrochemically oxidised in an electrolyte containing negatively charged species which are thereby caused to become incorporated into the polymer structure forming the film. Optionally, and again subsequent to separating the polymer film from the electrode in the region of the aperture or gap, the film may be electrochemically reduced in a solvent, for example in distilled water, so as to cause negatively charged species to leave the polymer structure forming the film and enter the solvent. Such treatments of the polymer film involving incorporation of such species into, and their removal from, the polymer structure are known as 'doping' and 'undoping'. The capability of altering the amount or concentration of a charged species present in the polymer film means that when the film is to be utilised in a gas sensor the sensitivity of the film to the target gas (ie. the gas to be sensed or detected) may be altered.

In order that the present invention may be more readily understood, reference will now be made, by way of example only, to the accompanying drawings, in which :-

Figure 1 shows in schematic form an example of a substrate on which a film of material is to be formed,

Figure 2 shows in schematic form one embodiment of apparatus for carrying out a method according to the invention,

Figure 3 is similar to Figure 1 but after the film material has been deposited on the substrate, and

Figure 4 shows a graph of test results which are illustrative of the response of the film as a gas sensor.

With reference to Figure 1, the substrate comprises a thin, small tile 1 of electrically insulating material, such as alumina, having an aperture 2 therein. The whole surface of the tile (i.e. both sides and all of the inner and outer edges) is sputtered with platinum except for the two tile areas 1a,1b which have been masked and which extend completely around the tile (i.e. across both sides and the inner and outer edges of the tile) in their respective regions on opposite sides of the aperture 2. Thus the platinum sputtered tile comprises two platinum areas 3a,3b (only those portions on upper surface 4 of the tile being shown) which are spaced apart from each other over the whole surface of the tile by means of the tile areas 1a,1b. The film is to be formed so as to bridge the

aperture 2 and extend over the spaced areas 3a, 3b of platinum on surface 4 of the tile.

With reference to Figure 2, the apparatus comprises a container 5 containing a pool of mercury 6, forming an electrode, on which floats an aqueous electrolyte solution 7 comprising potassium chloride and dissolved pyrrole monomer. A platinum wire 8 which connects the mercury to a source of electricity 9 is protected from direct contact with the electrolyte solution by a surrounding glass capillary tube 10.

The tile 1 is floated on the mercury with the surface 4 of the tile bearing the platinum areas 3a,3b facing upwards and exposed to the electrolyte solution. The mercury anode is thus in electrical contact with the exposed, upwardly facing platinum areas by way of the layer of platinum on the underside and edges of the tile. The platinum areas 3a,3b and the mercury together form a common electrode. A platinum mesh 11 forming the other electrode is immersed in the electrolyte solution above and opposite the tile.

In use, an electric current is passed through the two electrodes (i.e. the common 'mercury/platinum areas' electrode on the one hand and the platinum mesh on the other hand) and electrolyte solution such that the common electrode functions as an anode and the platinum mesh as

a cathode. As a result a poly-pyrrole is electrochemically deposited both on the exposed portions of the platinum areas 3a,3b on the tile and on the mercury surface inside or in the region of the aperture in the tile to produce on the tile a film 12 which also bridges the aperture. Platinum is particularly suitable metal in this connection as it neither forms an amalgam with the mercury nor dissolves in the mercury. However, other metals which are substantially inert to mercury may be used to form these electrically conducting areas on the surface of the tile.

When the electric current is turned off, the polymer film formed on the mercury electrode surface in the region of the aperture is separated intact from the mercury surface whilst remaining attached to the platinum areas on the surface of the tile to form the gas sensor component.

In the above Example, poly-pyrrole is also deposited on the mercury anode surface surrounding the tile and any excess polymer film extending beyond the outer edges of the tile may be trimmed off.

The conditions under which the above Example was conducted and the film thickness produced are set out below :-

Pyrrole Concentration	0.1 M
Potassium Chloride Concentration	0.1 M
Voltage	5 V
Initial Current	100 mA
Dimensions of tile	12mm x 12mm
Dimensions of central aperture in tile	5mm x 5mm
Final Current	18 mA
Period of Polymer Growth	20 mins
Film Thickness	100 microns
Distance from Cathode to Anode	1.5 cm
Temperature	$25^{o}C$

The following test illustrates the gas sensing property of a poly-pyrrole-film-covered substrate tile obtained in accordance with the above Example.

Over alternate periods of 5 minutes air or 1% ammonia/air (wt./wt.) mixture were passed at a flow rate of $150cm^3$/min over the polymer film. Thus, after each 5 minute period the gas flow was switched from the air to the ammonia/air mixture, or vice versa.

During the test the resistance of the polymer film was measured via electrical connections from the platinum electrodes to an ohmmeter.

The plot of resistance against time on the graph in Figure 4 shows the change in resistance of the polymer film in response to the different gases. It can be seen how the resistance of the film increases when ammonia is present.

Applicants have found that the above described method not only produces a polymer film which spans or bridges the aperture and is accessible from both sides but also gives thin, reproducible films which can give satisfactory repeatable conductivity results. Moreover, the method is capable of providing a relatively large area of polypyrrole film to act as a gas sensor and therefore be more sensitive compared with film produced by the prior art method described earlier, where only a relatively thin or strip of film acts as gas sensor proper. Examination by electron microscopy has shown the film produced by the above method to be much more uniform in texture than one produced by the earlier described prior art method.

CLAIMS

1. A method of forming a film of material on a substrate having an aperture or gap therein, comprising electrochemically depositing from an electrolyte a film of material onto an electrode on the substrate and onto an adjoining electrode which extends across the aperture or gap in the substrate such that the film adheres to, and bridges the aperture or gap in, the substrate, and then separating the deposited film and electrode in the region of the aperture or gap on which the film has deposited from each other to leave the film substantially intact, adhering to the substrate and bridging the aperture or gap in the substrate.

2. A method as claimed in claim 1, wherein the electrode in the region of the aperture or gap is formed by a surface region of a pool of mercury on which the substrate is supported and the electrolyte floats.

3. A method as claimed in claim 2, wherein the substrate floats on the mercury.

4. A method as claimed in any of the preceding claims, in which the electrode on the substrate comprises spaced electrical conductors over which the film forms.

5. A method as claimed in claim 4, wherein the spaced electrical conductors comprise areas where, prior to electrochemically depositing the film, electrically conducting material has been deposited on the substrate.

6. A method as claimed in any of the preceding claims, wherein the substrate is made of alumina.

7. A method as claimed in any of the preceding claims, wherein the electrolyte contains the monomer of an organic based unsaturated polymer and the organic based polymer is electrochemically deposited to form the film.

8. A method as claimed in claim 7, wherein the electrolyte contains ionic species which are incorporated in the electrochemically deposited film and are electrically balanced in the film by the presence of oppositely charged polymer components.

9. A method as claimed in claim 7 or 8, wherein the monomer is pyrrole and the organic based polymer is polypyrrole.

10. A method as claimed in claim 9, as dependent on claim 8, wherein the ionic species are chloride anions.

11. A method as claimed in any of claims 7 to 10,

wherein, subsequent to separating the film from the electrode in the region of the aperture or gap, the film is electrolytically oxidised in an electrolyte containing anions which enter and are incorporated into the polymer structure forming the film.

12. A method as claimed in any of claims 7 to 11, wherein, subsequent to separating the film from the electrode in the region of the aperture or gap, the film is electrolytically reduced so as to cause anions to leave the polymer structure forming the film.

13. A method as claimed in claim 1 and substantially as hereinbefore described with reference to the accompanying example.

14. A substrate having an aperture or gap comprising a film of material adhering to the substrate and bridging the aperture or gap therein, obtained by a method as claimed in any of the preceding claims.

15. A gas sensor incorporating a gas sensing component comprising a substrate as claimed in claim 14.